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(54) Title: THE METHOD AND DEVICE FOR PRODUCING HIGHER FULLERENES AND NANOTUBES (57) Abstract <p>A fullerene/nanotubes mixture is produced during a periodical pulsed auto-regulated action of the electric current arc-discharge in the multi-component hydrocarbon medium with limited fullerenes' solubility, besides, the action is continued until the medium dissolves C₆₀. Higher fullerenes absorbed by the ultra-thin graphite particles are separated from C₆₀ dissolved in the liquid medium by sedimentation, whereas the carbon nanotubes are separated from the ultra-thin graphite particles by treating with a boiling concentrated HN03 acid and by low speed centrifuging/acid mixture until the black sediment of the ultra-thin graphite particles is precipitated to the bottom. The periodically pulsed auto-regulated regime of the electric-current arc-discharge is performed by contact breaking an electric circuit due to lifting spherical contactors by gaseous products released during the action and by switching the circuit due to the contacts' going down under action of gravity.</p>		

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The Method and Device for Producing Higher Fullerenes and Nanotubes

The invention is related to chemical technologies, particularly to the field for the production of fullerenes and carbon nanotubes.

Fullerenes and nanotubes are the most desirable materials for basic researches in both chemistry and physics, as well as applied researches in electronics, non-linear optics, chemical technologies, medicine, and others.

The processes of producing new allotrope forms of carbon, fullerenes and nanotubes, are based on different methods of generation of a cool plasma of carbon clusters (such as a laser ablation of carbon-containing substances, a pyrolysis of hydrocarbons, or an electric arc discharge, etc), and clusters' crystallization to fullerenes and nanotubes under certain conditions. After which fullerenes are eluted from the soot by the use of any organic dissolvent (benzene, toluene, xylenes, carbon disulfide, etc)[1]. Nanotubes on the other hand are separated from the soot by the use of any oxidation process [2].

The processes of forming fullerenes and nanotubes are competitive and, therefore, it is possible to displace a balance in their output by changing conditions either of the generation process or crystallization. Increasing the pressure of a buffer gas (He or Ar) from 50 - 150 Torr, which is optimal for producing fullerenes, to 500 Torr leads to a preferential formation of nanotubes [3]. In addition, some metal catalysers (Co, Ni, Pt, Fe, etc) are added to an initial graphite, leads to a preferential formation of Single-Walled NanoTubes (SWNT)[4] with a yield upto 70% in case of a laser ablation of the graphite.

Several methods are used for producing SWNTs [4], each of which differs by a generation of the cool carbon clusters' plasma. Comparatively low outputs of SWNTs lead to very high prices of the SWNTs (\$1,000-10,000 per gram).

The process of producing higher fullerenes (the fullerenes higher than C70) is developed in less extent than the one for the classical production of, C60 and C70.

The main problem being a very low yield of the higher fullerenes, which for C74, C76, C78, and C84 is usually about 1-3% and less than 0.1% for C90, C94, C98 in comparison to the 10 - 40% of the classical ones[5]. As a result, available amounts of C90 and higher, are not enough to study their general properties.

Thus, a method and device is required for producing higher fullerenes and carbon nanotubes with an attainable technical result (greater amounts of higher fullerenes and nanotubes at a relative low cost), that is expressed in a preferable producing the higher fullerenes and in a simple separation of the nanotubes from the soot particles.

The existing method and device for producing fullerenes [6] suggests the following. That graphite electrodes be placed in a contained volume filled by He gas at a pressure of 50 -150 Torr. Under certain conditions (electric arc's current is up to 200 A and voltage in the range 5-20 V), evaporated graphite clusters can form fullerene molecules, mainly C60 (80-90%) and C70 (~10-15%) as well as small amounts of higher fullerenes (total sum is not exceeding 3 - 4%). High Performance Liquid Chromatography (HPLC) is required to separate individual fullerenes [7].

HPLC is characterised by a very low production of higher fullerenes and, as a result, market prices of the higher fullerenes are enormous, more than \$1,000-10,000 per gram (Aldrich catalogue, 1999). Therefore, this method and device is useless for producing higher fullerenes. Outputs of C76, 78, 84 for such a technology is about a couple of milligrams a day per processor, higher ones even less.

The use of both a relatively low arc currents and special metallic catalyzer is needed for producing one-walled carbon nanotubes with certain diameters. The maximal nanotubes' output achieved is 60% of the graphite material scraped from a cathode surface. The total nanotubes output is highly decreased during the separation of the nanotubes from the rest soot particles when an oxidation process with gases (oxygen, carbon dioxide) is usually used. Moreover, the separation process is rather long and complicated.

It is therefore necessary to find an approach, which allows a production of higher fullerenes and nanotubes with higher yields.

For the C74 fullerene such a way has been realised [8] by the use of a constant current arc-discharge in a liquid benzene and / or toluene medium, which dissolves fullerenes well. The dominant fullerene molecules were C50, whereas the concentration of C60 and C74 was comparable but 3 - 8 times less than that of C50. All produced fullerenes were dissolved in the medium and, after removal of non-dissolved soot particles (either by centrifugal or filtration), fullerenes were able to be separated by HPLC.

However, no fullerenes, greater than C74, and SWNTs were produced this way. The greatest problem of all the methods is the use of an electric arc discharge that provides a gap of constant value between the graphite rods. In observing Modak's method [8] a safety problem arose because of a release of huge amounts of gases (mainly, hydrogen and acetylene) in a process of cracking benzene/toluene.

The best solution regarding these problems is using an auto-regulated process of the electric arc, which periodically switched off and on an electric circuit.

The device and method for producing fullerenes [9] during a periodical pulsed auto-regulated action of the Electric-Current Arc-Discharged (ECAD) in natural liquid hydrocarbon mediums like diesel fuels, oils, etc. is the closest to our invention by a main point and attainable result. The pulsed auto-regulated regime of the ECAD, is performed by a contact breaking of the electric circuit. This is due firstly, to the lifting of a spherical graphite contactor by the gaseous products released during the action and secondly, by switching On the circuit due to the contactor's going down under action of gravity to two opposite-polarity graphite electrodes made as plates (see Fig.1).

The fullerene mixture is produced during the pulsed auto-regulated action of the Electric-Current Arc-Discharged (ECAD) in a multi-component hydrocarbon medium liquid. A pulsed character of the action (the ECAD current intensity varies from zero to j_{\max} and then to zero) allows the achievement of an optimal current intensity (j_{opt}) by choosing a maximum current intensity (j_{\max}) essentially more than the expected value of the optimal intensity (j_{opt}). It is important to note that, such an action avoids the over saturation of the arc gap by gaseous products.

The device and method mentioned above is able to produce a relatively high yield of higher fullerenes, i.e., C84 and C60 may be comparable.

However, fullerene outputs are low (about 10 mg per cycle per processor) because of a rapid improper erosion of a surface of the electrodes during the arc action (see drawing 1/4). As a result of this erosion, a cross section of the electric arc discharge is increased with time, reducing the intensity of the arc's current, and the temperature of the carbon clusters' plasma. After 5 -10 minutes of the processing, judging by the sizes of the electrodes and contactor, this reduction leads to the termination of the fullerene formation process. Since a minimum of the current intensity (about 100 A/cm²) is required to form C60/C70 and higher fullerenes in such a process.

In conclusion, light fullerenes (C28 to C50) and soot particles are mainly produced by this method, in turn reducing the yield of the higher fullerenes and C60. A prevailing of light fullerenes in comparison to C60 and higher fullerenes complicates a valid detection and separation of the higher fullerenes.

An absence of a buffer gas and a presence of oxygen (from air) are added factors that reduce fullerene/nanotubes yields.

Finally, an important factor reducing fullerene/nanotube yield is a prevailment of alkanes/alenes and cycloalkanes (C_nH_{2n+2}/C_nH_{2n} and C_nH_{2n}) in the natural liquid mediums (i.e. petrol consisting of 1.5-6% of pentane, isopentanes 0.5-2%, hexane 3-9%, isohexane 1-4%, heptane 3-11%, isohexane 3-6%, octane 5-9%, isooctanes 5-9%, nonane 3-6%, isononanes 4-9%, cyclopentane 0.1-0.5%, methylcyclopentane 2.5 - 5%, cyclohexane 2.5-7%, naphthenes (C_7H_{14}) 10-20%, naphthenes (C_8H_{16}) 7-15%, naphtene C_9H_{18} 5-14%, benzene 0.2-2%, toluene 1-5%, xylenes 2-7%). During cracking, alkanes/alenes produce two times greater amounts of hydrogen in comparison to aromatic hydrocarbons (nearly, C_nH_{n-x}), and it is known that superfluos amounts of hydrogen restrain forming fullerenes/nanotubes.

In order to achieve a technical result, in other words great amounts of the higher fullerenes and carbon nanotubes at a relatively low cost, it is necessary to increase the relative yield of the higher fullerenes / nanotubes and omit HPLC as a method of the fullerene separation. Thus, the problem of the conception of the method and device for producing higher fullerenes / nanotubes with an attainable technical result, great amounts of the higher fullerenes/nanotubes with a relatively low cost, is maintained.

A solution of the method and device problems for producing higher fullerenes and nanotubes is achieved by two variants.

The first variant is only used if it is possible to compose the liquid of aromatic hydrocarbons which dissolve a required fullerene better than other fullerene including C60. It is known [10 - 13] that aromatic liquids (benzene, toluene, xylenes, etc) dissolve C60 and higher fullerenes differently, i.e. at room temperature (20°C) toluene dissolves C60 (~2.8 g/l) two times better than C70 (~1.4 g/l), but o-xylene does it differently, solubility of C60 is 5.2 g/l whereas of C70 is 14.3 g/l. As a rule, solubility of C60 reduces when an increase of temperature occurs, whereas solubility of higher fullerenes increases with temperature increase.

Moreover, the fullerene/nanotube mixture is produced with a presence of argon gas in a multi-component aromatic hydrocarbon liquid which dissolves the required higher fullerenes better than other fullerenes including C60, furthermore, the action is continued until the liquid dissolves the higher fullerenes. In that case, the required higher fullerene completely forces out other fullerenes (including C60) from the solution

(liquid) to a soot / nanotube precipitation due to better solubility. In this case it is sufficient to separate the treated liquid (mostly containing the higher fullerene) from the soot / nanotube precipitation (with adsorbed the rest fullerenes including C60) by filtering through Whatman filters.

The liquid is then filtered through a certain layer of molecular sieves with diameters of pores of 8 -10 Angstroms, which selectively adsorb light fullerenes (less than C60, namely, C28-C50). Taking into consideration the lack of information regarding the solubility of light fullerenes, the molecular sieves completely adsorb any molecules with sizes less than 7 Angstroms. The latter do not adsorb molecules with sizes equal or more than 7 Angstroms, i.e., C60 and higher fullerenes are not adsorbed by the molecular sieves. The "cleaned" liquid is then evaporated in vacuum to form a crystalline powder of the higher fullerene.

By using the Whatman filters, the sediment is dried in a vacuum oven and cleaned by washing. For washing, certain organic solvents which have a minimal solubility of fullerenes are used, the best of which are methanol (solubility of C60 is about 0.035 mg/l), acetone (1 mg/l) and pentane (5 mg/l).

Subsequently, the remaining fullerenes are eluted from the cleaned sediment by benzene, toluene, xylene, etc. The formed solution is evaporated in vacuum to form a C60 and higher fullerenes with a small admixture of the required higher fullerene crystalline powder.

The nanotubes in turn are separated from the remaining soot by a specific oxidation process. We suggest using a treatment of the carbon (soot/nanotubes) remainder. This is done by adding and boiling concentrated nitric acid during 1-2 hours in order to open the nanotubes' caps and thus separating the nanotubes from the soot particles. Finally, a centrifugal with a low rotation velocity ($500-1,000 \text{ min}^{-1}$) is used to separate the nanotubes from the rest soot particles.

Under such a separation the rest soot particles, which are spherically shaped with sizes (1,000-2,000 Å) larger than those of the nanotubes lumps (300-1,000 Å), are precipitated in the first turn forming a black sediment at the bottom of the vials, whereas, the nanotubes form a dark- orange gel with the acid. One can separate this gel into some fractions by taking part of the gel layer-by-layer. Each of the gel fractions contains lumps of SWNTs with nearly the same sizes. Such a separation is checked simply and obviously. Therefore one can have an additional product, carbon nanotubes, producing higher fullerenes by our method and device.

The second variant is destined if it is impossible to compose a liquid of aromatic hydrocarbons, which dissolves a required higher fullerene better than other fullerenes including C60.

In this case the fullerene mixture is produced in a multi-component aromatic hydrocarbon liquid which dissolves the required higher fullerenes less than other fullerenes including C60. The action is continued until the liquid dissolves the remaining fullerenes including C60 up to a moment when their concentration becomes equalled to a limit of their solubility in the liquid.

In these conditions, other fullerenes (including C₆₀) force out the most part of required higher fullerenes to a soot/nanotube precipitation, therefore, the higher fullerenes might be separated from the rest fullerenes by using Whatman filters.

After drying and cleaning the separated soot sediment (as the above mentioned method)), the required higher fullerenes are eluted from the sediment by a certain dissolvent (benzene, toluene, xylene, chlorobenzene, etc) with the help of a Soxhlet extractor.

Thus, these two variants of the method allow us to produce any higher fullerene and separate it from the rest fullerenes by composing a liquid with higher or lower solubility of the higher fullerene than that of others.

These variants are realised by the device as following (see a drawing at 2/4):

The device differs from the prototype by a geometry of the electrode system: cylindrical graphite pipes (electrode A) are installed axially in vertical cylindrical openings of a cylindrical graphite matrix (electrode B) and spherical graphite contactors are placed above the pipes. One notices that such a geometry maintains a constancy of the arc discharge cross section (therefore, constancy of the arc temperature) as it is defined by a cross section of the pipes, which is kept constant from the top to bottom.

With this pipe-geometry of electrode A, it becomes possible to pump Argon gas through the pipes to a space of the arc discharge. It is performed before and during the action of the arc discharge, thus allowing the removal of oxygen from the liquid, and avoiding fullerenes' oxidation, and thus creating optimal conditions for carbon clusters annealing to fullerenes / nanotubes.

The body is filled by the hydrocarbon liquid to a level above the contactors to provide a maximum average duration of individual acts of the arc discharge. It allows increasing yields of the higher fullerenes because an interval, when the arc temperature is maximum, becomes greater.

An example of the invention's realisation:

Both variants have been tried.

The device was made as following: Graphite pipes (electrode A) with a length of 50mm and external/internal diameters of 4 and 2 mm, correspondingly, Spherical graphite contactors with a diameter of 12.5 mm, Vertical cylindrical openings of the graphite matrix (electrode B) with a diameter of 13.5 mm. A cylindrical stainless steel body was filled by a liquid (based on benzene solution of some aromatics like naphtaline, toluene, and xylenes) to a level of 50 cm above the contactors. Such a level provided a maximum duration of the arc action as it was found in our experiments. Pure argon gas was pumped through the graphite pipes (electrode A) before the action (to remove air from the body and liquid) and during the action creating optimal conditions for carbon clusters annealing to fullerenes/nanotubes. Arc's cross sections about 3-4 mm² and the intensity of arc's current in the range of 100—400 A/cm². The duration of the action (4-6 hours) depends on the type of a required higher fullerene and, therefore, on the variant of the method and nature of the liquid, which are used for producing fullerenes/nanotubes.

By using the first variant, we produced a mixture of higher fullerenes (see HPL-Chromatograms and Mass Spectrum at 3/4), mainly containing C98 (~80%) with nearly 3% of C76 and ~15% of C78, with a total output in the range of 2-20 g per a processor per a cycle (of 5 hours' duration).

The second variant was used to produce a fullerene mixture, mainly containing C98 (~70%) with nearly 20% of C76 and about ~10% of C60 (see MS spectra at 4/4), with a total output in the range of 1-10 g per a processor per a cycle (of 5 hours' duration).

An additional output of the nanotubes is estimated in the range of 100-300 grams per a processor per a cycle. These nanotubes appeared as short (300-1,000 Å) ropes of SWNTs with average diameters of individual nanotubes in the range of 10-15 Å as it was estimated by Kr adsorption-desorption processes using our original XRF-based technique [14].

Consequently, the technical result of our invention, great amounts of the higher fullerenes and nanotubes with a relatively low cost was achieved.

References:

1. R. E. Smalley. From Balls to Tubes to Ropes: New Materials from Carbon – in Proc.of American Institute of Chemical Engineers, South Texas Section, January Meeting in Houston - January 4, 1996
2. P.M.Ajayan.et al, *Nature*. 1993, V.362, p.522
3. T. Guo. et al, *Chem. Phys. Lett.*, 1995, V.243, p.49
4. Andreas Thess, et al, *Science*, 273. 483-487 (July 26, 1996)
5. K.S.Khemani, et al, *J. Org. Chem.*. 1992, V.57, p.3254
6. W. Kraechmer et al, *Nature*, 1990. V.347, p.354
7. F. Diederich. et al, *Science*. 1991. V.252. p.548
8. D.K.Modak et al. *Indian J.Phys.*, 1993, V.A67, p.307
9. A.P.II'in, Yu.A.Kracnyatov, G.A.Volostnov, V.T.Galeev. ICI C01 B31/00. The device and method for producing fullerenes - Application to a Russian Patent (Tomsk High Voltage Institute). Priority from September,1997
10. R.S.Ruoff, et al. *J. Phys. Chem.* 1993, V.97, p.3379
11. M.T.Beck, G.Mandi. *Fullerene Sci. Technol.* 1996, V.3, p.32
12. N.Sivaraman, et al. *J. Org. Chem.* 1992, V.57, p.6007
13. X. Zhou, et al. *Fullerene Sci. Technol.* 1997, V.5(1), p.285
14. V.A.Ryzhkov – in Abstracts of Intern. Workshop on Fullerenes and Allotropes of Carbon, IWFAC'99, 3-8 October 1999, St Petersburg, Russia

Claims:

1. The method for producing higher fullerenes and nanotubes, including forming and annealing carbon clusters during a pulsed auto-regulated action of the electric-current arc-discharge between graphite electrodes loaded inside a hydrocarbon liquid, extraction and separation of the fullerenes and nanotubes, differs by, that the fullerene/nanotube mixture is produced at arc's current intensity of 100-400 A/cm² and voltage 20-50 V with a presence of argon gas in an aromatic hydrocarbon liquid which dissolves the required higher fullerenes better than other fullerenes including C₆₀, besides, the action is continued until the liquid dissolves the higher fullerenes, after that the treated liquid is filtered through Whatman filters, separating a nanotube/soot mixture with adsorbed the rest fullerenes including C₆₀, and then through a layer of molecular sieves with diameters 8Å and 10 Å, separating low fullerenes less than C₆₀, and evaporated in vacuum, forming a crystalline powder of the higher fullerenes, besides, after cleaning the nanotube/soot sediment by washing with methanol or acetone, the rest fullerene mixture is eluted from the cleaned sediment by any certain dissolvent and evaporated in vacuum, forming a crystalline powder of the rest fullerene mixture, besides, the nanotubes are separated from the rest carbon particles by treating with a boiling concentrated HNO₃ acid during 1-2 hours and, afterwards, by low speed centrifugal of the carbon/acid mixture until the black sediment of the soot particles is precipitated to the bottom
2. The method by p.1, differs by, that that the fullerene mixture is produced in the liquid which dissolves the required higher fullerenes less than other fullerenes including C₆₀, besides, the action is continued until the liquid dissolves the rest fullerenes including C₆₀, after that the treated liquid is filtered through Whatman filters and, after cleaning the soot sediment, the required higher fullerenes are eluted from the sediment by any certain dissolvent with a Soxhlet extractor
3. The device for producing higher fullerenes and carbon nanotubes, including a hermetically sealed body, in which opposite-polarity graphite electrodes (electrode A and B) are installed and connected to a power supply switched on/off by spherical contactors, which have possibility for retrogressive movement along the round vertical opening and around its geometrical centre, differs by, that cylindrical graphite pipes (electrode A) are installed axially in vertical cylindrical openings of a cylindrical graphite matrix (electrode B) and spherical graphite contactors are putted above on the pipes, besides, argon gas is pumped through the pipes (electrode A) before the action and during the arc discharge process and the body is filled by the liquid to a level above the contactors to provide a maximum average duration of individual acts of the arc discharge.

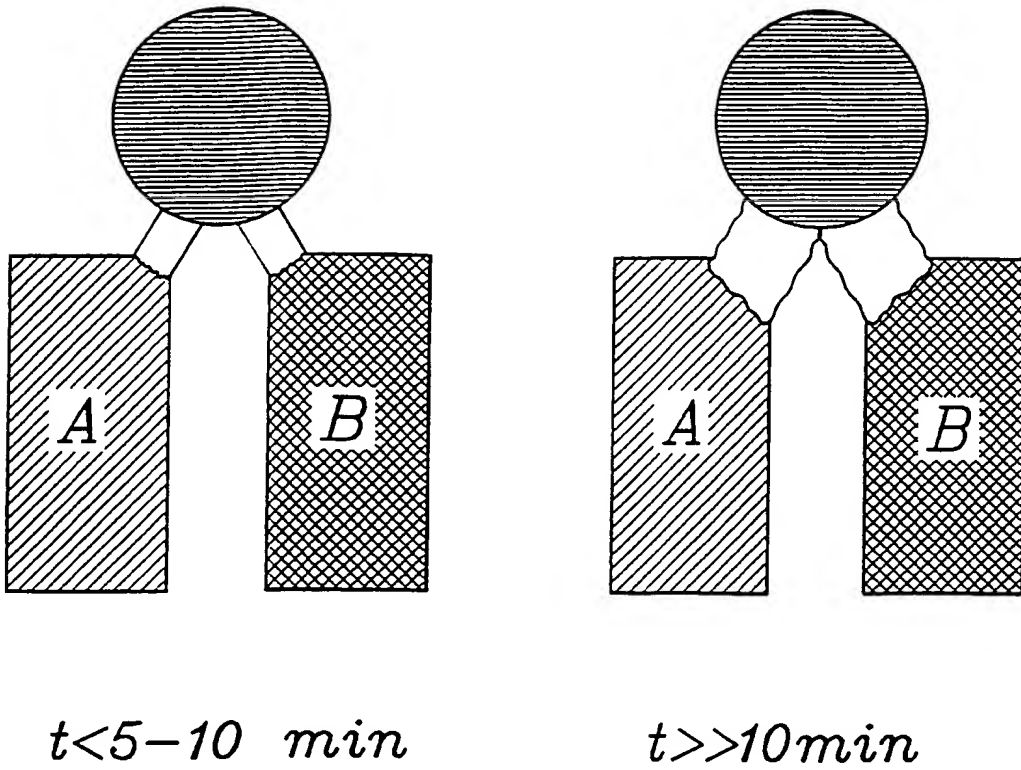
Arc's cross sections

FIG.1 Erosion of the flat electrodes under arc's action

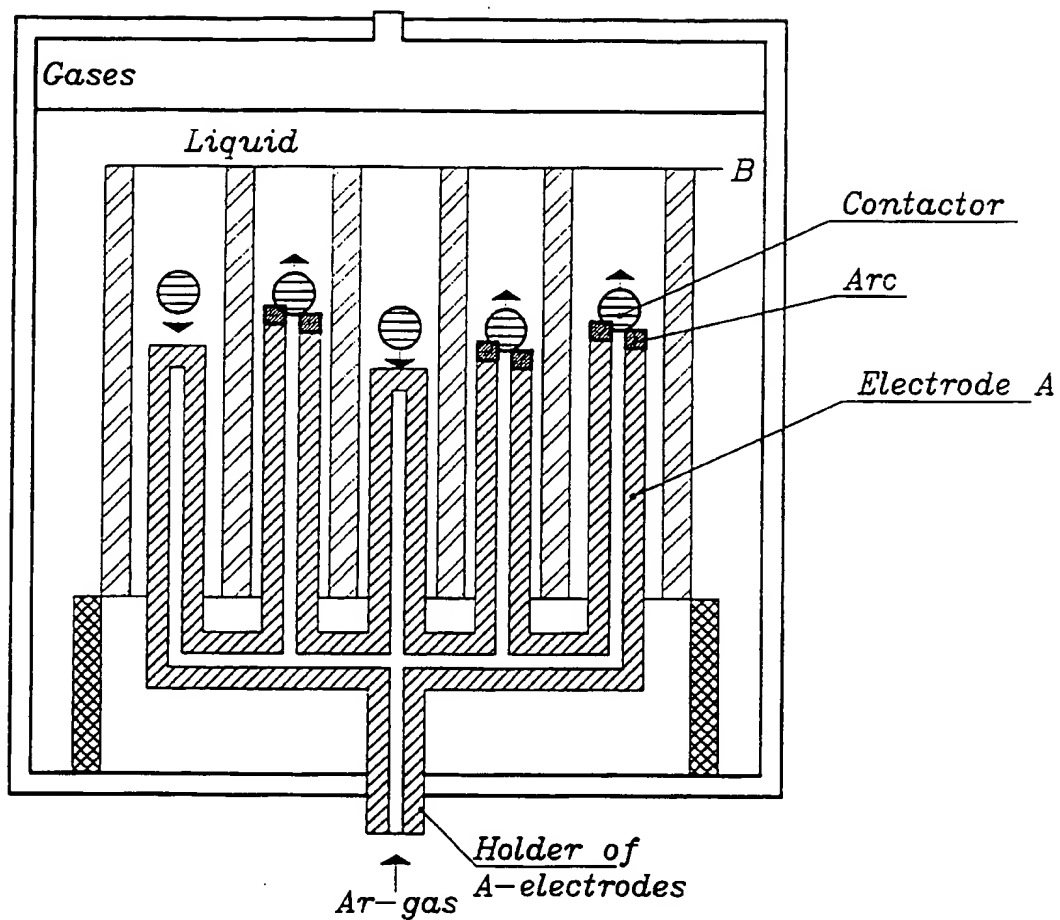


Fig.2 Scheme of the device for producing higher fullerenes and carbon nanotubes

